UNCLASSIFIED

NYO-5219

CHEMISTRY

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

UNCLASSIFIED

0
UNITED STATES ATOMIC ENERGY COMMISSION

THE DETERMINATION OF URANIUM IN K-65
(GANGUE LEAD CAKE)

By
John W. Stevenson

Photostat Price \$ 1.80

Microfilm Price \$ 1.80

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

January 1948

Mallinckrodt Chemical Works, St. Louis

Technical Information Service Extension, Oak Ridge, Tenn.

This document is
PUBLICLY RELEASABLE

Hugh Kinser
Authorizing Official

Date: 9-25-11

406 001

CLASSIFICATION CANCELLED
DATE 12-12-53
by The Atomic Energy Commission
#4 Canell
Chief, Declassification Branch

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THE DETERMINATION OF URANIUM IN K-65 (GANGUE LEAD CAKE)

By John W. Stevenson

Introduction

The problem is to determine 1 to 3% X in the presence of 1 to 3% Mo, V, Ba, Mg, Na, Sr, Ni, Ca, Co, Fe, Zr and much larger amounts Pb, Si, Al and $\text{SO}_4^{=}$.

Summary

The major problems in this determination are the extraction of X from the sample and the isolation of the extracted X. The application of various analytical methods to these two problems indicates that the current method of analysis yields values which may be as much as 15% high.

The current method of analysis is subject to positive and negative errors. The magnitude of these errors varies with techniques and with sample composition. The recommended method, although longer, is believed to be free of these errors, but a radical change, say 100 fold, in the composition of the sample would certainly require further investigation.

Conclusions

The current method of analysis contains positive and negative errors.

The values obtained by the current method may be as much as 15% high.

The amount of X escaping detection in the proposed method is probably less than 0.25 mg, a quantity seldom greater than 1% of the X measured.

When the initial ratio of $\text{SO}_4^{=}$ to X approaches 90, X is incompletely extracted under the proposed conditions. The loss is greater as the $\text{SO}_4^{=}$ to X ratio becomes larger. The ratio of $\text{SO}_4^{=}$ to X obtained in the recommended procedure for K-65 is approximately 10. Hence X is completely extracted. If small amounts of X, say 1 mg, are to be extracted, the effect of $\text{SO}_4^{=}$ to X ratio should be checked.

The removal of Mo was satisfactory. If the method is to be extended to samples where the Mo to X ratio is very high, i.e., 10 to 100, the Mo removal

should be investigated further. This work should be done on the sample since Mo complexes may be a factor.

Recommended Method

Dry K-65 for 24 hours at 100–110°C. Weigh 2 gm (± 0.01 gm) on a torsion balance and transfer to 150cc beakers. Add 20cc concentrated HNO_3 and 20cc water. Cover with a tight cover glass and boil at least 30 minutes, keeping the volume constant by addition of water. Cool somewhat, to avoid attacking the filter paper, and filter on S and S Blue Ribbon paper. Wash twice with 5cc portions of water. Puncture the filter paper and transfer the residue to the original beaker using as small a volume of water as possible (about 30cc). Add 20cc concentrated HNO_3 . Cover with a tight cover glass and boil 30 minutes. The volume should be kept to 40cc by addition of water. Cool as before and filter into the first filtrate. Discard the residue. Concentrate the combined filtrates to 70 to 80cc but not much further or insoluble salts precipitate. Separation of a solid phase is not known to be harmful but should be avoided. Transfer the solution to a 500 ml glass stoppered separatory funnel filled $\frac{3}{4}$ full with NH_4NO_3 A.R. Continue the analysis as in Reid's method for R.P., i.e., 5 ether extractions, evaporation of the ether, fuming with HClO_4 , HNO_3 , Na_2CO_3 , buffer, H_2O_2 , read % at about 425 mu.

Experimental Notes and Data

The standard sample of K-65 used in this work was a composite which had been dried and mixed on rollers for four hours. Portions removed for analysis were dried at least 24 hours at 100–110°C and were then stored in a CaCl_2 desiccator.

The possibility of missing large quantities of X when using the current procedure required investigation and the true value of X was needed. The answers to these problems appear as the problems of extraction, isolation, and measurement of X are discussed. It will be observed that values of X on the standard sample by the current method ranged from 1 to 1.3% and that no method of attack gave values higher than 1.45%. Hence the current procedure appears to give the right order of magnitude for X. The true value of X for the standard sample is believed to be 1.05%. The data and discussion to support this belief will follow. It seemed impossible to get precise values for X by the current procedure. Table I lists some values obtained with brief notes.

Table I—X in K-65 by Current Method

Percent X	Modification
1.26	
1.14	
1.10	
1.10	
1.11	
1.27	50cc water, solid Na_2CO_3
1.12	do
1.33	cold acid, solid Na_2CO_3
1.34	do
1.05	15 minutes in cold acid, then boil
1.08	do
1.03	do
1.01	do
0.92	do
1.13	do
0.84	boil acid 2 minutes, dilute, boil 5 minutes
0.93	do
0.91	do
0.94	do
0.96	do

The variations observed are quite unsatisfactory.

Table II gives the values of X by various methods of attack.

Table II—Method of Decomposition vs. Percent X

Number	Method	Percent X
1	Na_2CO_3 fusion, Reprecipitations	1.36
2	do	1.43
3	Na_2CO_3 fusion	1.33
4	do	1.30
5	HCl digestion, Na_2CO_3 digestion	1.18
6	do	1.10
7	do	1.07
8	HCl digestion	1.09
9	do	1.05
10	do	1.04
11	H_2SO_4 digestion, Na_2CO_3 digestion	0.96
12	do	0.97
13	do	0.90
14	HNO_3 cold, 15cc Na_2CO_3 T.S. cold	0.91
15	HNO_3 cold, 20cc Na_2CO_3 T.S. cold	0.87
16	HNO_3 cold, 25cc Na_2CO_3 T.S. cold	0.87

All measurements of X were by the $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}_2$ method at 425 mu. In the Na_2CO_3 fusions, Nos. 1 and 2, Table II, all acid insoluble residue were fused at least twice and all precipitates formed in solutions found to contain X were re-dissolved and reprecipitated until the solutions did not contain X. This was found to be necessary. The agreement among 1, 2, 3 and 4 is therefore surprising since the precautions of resolution and reprecipitation were not observed in 3 and 4. It will be noticed that HCl and H_2SO_4 digestions offer no advantage over HNO_3 .

Table III gives the values of X obtained by successive passes through the current procedure, i.e., the residues were carried through the procedure again.

Table III—X by Multiple Application of Current Procedure

Sample	1 pass	2 passes	3 passes	4 passes
Standard		1.21% X	1.24% X	
Standard		1.15% X	1.19% X	
Standard		1.13% X	1.24% X	
Standard		1.14% X	1.18% X	
16608	1.22% X	1.97% X	2.21% X	2.23% X
16608	1.63% X	1.99% X	2.13% X	2.17% X
16670	1.22% X	1.52% X	1.64% X	1.65% X
16670	1.19% X	1.50% X	1.56% X	1.60% X
16831	0.95% X	1.36% X	1.47% X	1.49% X
16831	0.13% X	1.12% X	1.43% X	1.47% X

An inspection of the data of the first three tables shows that no method gave precise values for X. Data which will follow show that X can be extracted completely with acid, but that variable amounts of interfering substances are also extracted. Since these interfering substances are measured as X in the current procedure, the X appears to vary markedly with the conditions of digestion.

In Huston's report on the colorimetric $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}_2$ method for X he notes positive interference, when measuring X at a concentration of 0.01%, of Mo and V in concentrations of 0.001% and of Cr and Ag in concentrations of 0.0001%. He observed fading and negative interference in the same solution when Cu was present in concentrations greater than 0.0001 to 0.0002%. A spectrographic analysis of the standard K-65 sample is summarized in Table IV.

Table IV—Spectrographic Analysis of Standard K-65

Found	Element
VS	Si
S	Al, Mo, Pb, Ti
M	Ba, Mg, Na, Si, Ni, Th ⁺ , U, V
W	Ca, Co, Fe, Zr
VW	Cu and others
T	Ag and others

*Identification not positive.

For the complete report see No. 4-7465 or Spectrographic Laboratory No. 4178 or Plate No. D 793-B. The interference from Mo, V, and possibly Cu, Cr, and Ag is to be expected.

It was thought desirable to determine the X lost by adsorption on the PbCO₃ precipitate. Table V gives the percent X in the first acid extract of a sample, in the PbCO₃ separated from the first acid extract, in the second extract, and in the PbCO₃ separated from the second acid extract.

Table V—X Losses in Digestion and Adsorption

	Percent X
1st Acid Extract	0.96
1st Acid Extract	1.00
PbCO ₃ from 1st Acid Extract	0.02
PbCO ₃ from 1st Acid Extract	0.07
2nd Acid Extract	0.04
2nd Acid Extract	0.03
PbCO ₃ from 2nd Acid Extract	0.03
PbCO ₃ from 2nd Acid Extract	0.01

Apparently some X is lost on the PbCO₃ precipitates by adsorption.

Table VI lists the % X, % Mo, % V, % Cr, and % Cu in the solutions obtained by two passes through the current procedure.

Table VI—Solutions Obtained by Current Method

Element	1st Pass	2nd Pass	Total	Solution Concentration
% X	1.14	0.10	1.24	0.0248
	1.25	0.10	1.35	0.0270
	1.18	0.22	1.40	0.0280
% Mo	0.73	0.33	1.06	0.0212
	0.13	0.40	1.53	0.0306
	0.73	0.76	1.49	0.0298
% V	0.03	0.03	0.06	0.0012
	0.10	0.04	0.14	0.0028
	0.04	0.05	0.09	0.0018
Cr ppm	0.5	1.5	2.0	0.04
	1.0	1.0	2.0	0.04
	0.5	4.0	4.5	0.09
Cu ppm	88	75	163	3.3
	75	50	125	2.5
	25	lost		
Ag ppm	40			0.8
	50			1.0

X was determined by the $\text{Co}_3^{++}-\text{H}_2\text{O}_2$ method (Black Book under K-65) and is high due to interference of Mo. Mo was determined by the thiocyanate-stannous chloride method using butyl acetate as a solvent (Black Book under Chemical 6AAA). V was determined by the phosphotungstate method and may be about 5% high due to the interference of Mo. (Sandell, Colorimetric Metal Analysis, P 440-443). Cr was determined by the diphenylcarbazide method and is probably quite high due to the interference of V. (Sandell, Colorimetric Metal Analysis, P 191-195). Cu was determined by the dithizone method and is high due to interference of Ag and Pd. (Sandell, Colorimetric Metal Analysis, p 218-220 mixed color method). Ag was determined by the cupric dithizone method and is high due to the interference of Pd. (Sandell, Colorimetric Metal Analysis P 399). From these data and Huston's, it is apparent that Mo interferes seriously while the interference of V, Cr, and Ag is slight. It was decided to include separations to remove these interferences.

H_2S precipitation was tried. The results are shown in Table VII. Conditions could probably be adjusted to effect removal of Mo, Cu and Ag. The solutions faded less than they normally do. The difference was not pronounced but probably indicates Cu removal. The lower values of X might mean removal of Mo and Ag. V and Cr are not removed. Mo is difficult to remove as sulfide with a single precipitation and X losses due to adsorption would be possible.

Addition of Pb and Ag salts to the acid extract and removal of the excess as carbonate or sulfide was tried. The results appear in Table VIII.

Table VII—H₂S Separation of Mo, Cu and Ag From X

Sample	Conditions	Percent X
Standard	hot pH 1	1.04
Standard	hot pH 1	0.96
Standard + 0.25% X	hot pH 1	1.23
Standard + 0.25% X	hot pH 1	1.11
Standard	hot pH 2-3	0.97
Standard	hot pH 2-3	0.91
Standard	hot pH 2-3	1.37
Standard	HCl, hot pH 2-3	1.05
Standard	HCl, hot pH 2-3	1.09
Standard	HCl, hot pH 2-3	1.11
Standard + 1% V	HCl, hot pH 2-3	1.24
Standard + 1% V	HCl, hot pH 2-3	1.28
Standard + 1% V	HCl, hot pH 2-3	1.28

Table VIII—Ag and Pb Salts as Precipitants

Sample	Precipitant	Mg X	Percent X
10mg X + 10mg Cr	AgNO ₃ + H ₂ S	12.9	
10mg X + 10mg Cr	AgNO ₃ + H ₂ S	11.2	
10mg X + 10mg V	AgNO ₃ + H ₂ S	8.8	
10mg X + 10mg V	AgNO ₃ + H ₂ S	8.8	
10mg X + 10mg Mo	AgNO ₃ + H ₂ S	10.7	
10mg X + 10mg Mo	AgNO ₃ + H ₂ S	9.3	
10mg X + 10mg Cu	AgNO ₃ + H ₂ S	9.1	
10mg X + 10mg Cu	AgNO ₃ + H ₂ S	9.1	
Standard	AgNO ₃ + H ₂ S		0.17
Standard	AgNO ₃ + H ₂ S		0.38
Standard	Pb(NO ₃) ₂ + Na ₂ CO ₃		0.86
Standard	Pb(NO ₃) ₂ + Na ₂ CO ₃		1.00
Standard + 0.5% X	Pb(NO ₃) ₂ + Na ₂ CO ₃		1.21
Standard + 0.5% X	Pb(NO ₃) ₂ + Na ₂ CO ₃		1.27
Standard + *	Pb(NO ₃) ₂ + Na ₂ CO ₃		0.28
Standard + *	Pb(NO ₃) ₂ + Na ₂ CO ₃		0.43

*10mg Cr + 10mg Mo + 10mg V + 10mg Cu.

Adsorption errors are so large that this method is useless.

Reid, in his R.P. report, describes a set of conditions which gives complete extraction of X by ether from $\text{NH}_4\text{NO}_3\text{-HNO}_3$ solution. The X recovery in the presence of various amounts of SO_4^- was checked in this study. Results are given in Table IX.

Table IX—Effect of SO_4 on Ether Extraction of X

Mg X added	Mg SO_4^- added	Ratio SO_4^- to X	Mg X Found
25	1840	74	25.3
10	920	92	9.8
10	1840	184	8.8
10	3680	368	8.8
10	9200	920	5.1

Apparently X is not completely extracted by ether under the test conditions if the initial ratio of SO_4^- to X is much greater than 90. Digestion conditions recommended for the present K-65 give 86 to 104mg SO_4^- or a SO_4^- to X ratio of about 5 to 10. Extraction is complete. If small amounts of X are to be extracted, say lmg., this problem of SO_4^- interference would require investigation.

Ether extraction on digestions of K-65 was tried. The results for X are given in Table X.

The amount of Mo in the ether extract was found to be 0.56 mg and 0.68 mg or half the amount that would interfere. If the Mo to X ratio increases greatly, say 10 or 100 fold, and particularly if the amounts of X become quite small, say 1 mg in a 2 gm sample, the degree of separation from Mo will require investigation. Since the type of Mo compound present in the sample will probably determine the extent of ether solubility, the reinvestigation should be done on the new type sample.

On the basis of the data of Table X it appears that two successive digestions with 20cc HNO_3 and 20cc water at boiling for 30 minutes will extract the X. The acid suspensions must be filtered before ether extraction or troublesome emulsions result. The HClO_4 fuming gives slightly lower results and since organic contamination is always possible this step should be included. Huston has shown that NaClO_4 does not interfere with the measurement of X by the $\text{CO}_3^{--}\text{H}_2\text{O}$ method.

0.1mg X can be detected by the $\text{CO}_3^{--}\text{H}_2\text{O}_2$ reagent but quantities smaller than 0.25mg cannot be measured with much precision. This amount of uncertainty seldom exceeds 1% of the X measured.

As a summary, the values obtained by multiple acid extraction with and without ether extraction are compared to the reported values on several samples in Table XI.

Values obtained by the current procedure may be as much as 15% high.

Table X—X by Ether Extraction of Standard K-65 Sample

	Percent X
1. Boil. 20cc HNO ₃ . No HClO ₄	1.17
2. Boil. 20cc HNO ₃ . No HClO ₄	1.17
3. Cold. 20cc HNO ₃ . Extract Suspension	0.79
4. Cold. 20cc HNO ₃ . Extract Suspension	0.79
5. Boil 15 minutes. 20cc HNO ₃ . No HClO ₄	1.14
6. Boil 15 minutes. 20cc HNO ₃ . No HClO ₄	1.22
7. Current procedure. Extract. HClO ₄	1.04
8. Current procedure. Extract. HClO ₄	1.13
9. 3 passes 20cc HNO ₃ + 20cc H ₂ O. HClO ₄	1.05
10. 3 passes 20cc HNO ₃ + 20cc H ₂ O. HClO ₄	1.05
11. Standard. 20cc HNO ₃ . HClO ₄	1.07
12. Standard. 20cc HNO ₃ . HClO ₄	1.03
13. Standard. 20cc HNO ₃ . 2 passes. HClO ₄	1.09
14. do	1.05
15. 16670. 20cc HNO ₃ . 1 pass. HClO ₄	1.42
16. do	1.42
17. 16670. 20cc HNO ₃ . 2 passes. HClO ₄	1.45
18. do	1.43
19. 16608. 20cc HNO ₃ . 1 pass. HClO ₄	1.99
20. do	1.96
21. 16608. 20cc HNO ₃ . 2 passes. HClO ₄	2.01
22. do	1.99
23. 16831. 20cc HNO ₃ . 1 pass. HClO ₄	1.28
24. do	1.27
25. 16831. 20cc HNO ₃ . 2 passes. HClO ₄	1.30
26. do	1.29

Table XI—X by several methods

Sample	Lab. Value	No Ether Extraction*	Ether Extraction*
Standard		1.21	1.07
16608	2.60	2.20	2.01
16670	1.48	1.63	1.44
16831	1.43	1.48	1.30

*Average of duplicate determinations.

466 110